

## Conference Paper

# Research to Develop a Promising Technology for the Joint Disposal of Man-made Wastes

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## Abstract

The main components of RM are: Fe (35.7 %) in the form of hematite and complex hydroaluminatation, Ca (11.0 %) in the form of calcite and hydro-aluminosilicates, Al (6.8 %) and Si (4.7 %) in the composition of hydroaluminatation, Na (2.8 %) in the form of hydroaluminatation, carbonate and hydroxide, Ti (2.5 %) in the form of rutile. The main components of the OMS are: Fe (71 %) in the form of magnetite, wustite and hematite with a very small amount of fayalite. The contents of Si (in the form of quartz), Al and P (non-forming phases) are within 1–3 %. Granulometric composition of RM is characterized by high dispersion. With an average diameter of 1.6  $\mu\text{m}$ , all particle sizes are in the range of 0.5–12  $\mu\text{m}$ . Granulometric composition of OMS is characterized by complexity. With an average diameter of 8.6  $\mu\text{m}$ , maxima of 0.9  $\mu\text{m}$  and 15  $\mu\text{m}$  and a minimum of about 1.2  $\mu\text{m}$  are observed in the particle size distribution. The specific surface area of the materials is equal to RM 23.7  $\text{m}^2/\text{g}$ , and OMS – 1.9  $\text{m}^2/\text{g}$ . The change of waste properties after exposure to aqueous solutions of alkalis and acids neutralizing the effect of organic (OMS) and alkaline (RM) surface compounds was studied. Neutralization of aqueous suspension with HCl solution leads to removal of alkaline film from the surface. As a result of the impact of reagents, there is a decrease in the content of water-soluble components in the processing products. At the same time, the average particle sizes of RM and OMS increase to 2 and 14  $\mu\text{m}$ , respectively, and the specific surface area to 25.7 and 2.3  $\text{m}^2/\text{g}$ . The distribution of particle size of RM is almost constant, and the OMS is approximately 5 and 10 % of the smoothed maximum and minimum in the area of at least 0.5 and 15  $\mu\text{m}$ .

**Keywords:** red mud, oiled mill scale, chemical, phase, granulometric, composition, specific surface.

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## 1. Introduction

Currently, the red mud (RM) from processing bauxite, including the Urals factories are not fully utilized and accumulate in the sludge. RM is causing serious environmental hazards and economic problems. In particular, the mass storage RM Urals aluminium factories according to different sources varies from 100 to 300 million tons. One of

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the most difficult tasks in RM utilization of sludge is high humidity (not less than 50 %). Decrease of humidity to the bulk state produced virtually no because of their poor filterability, which makes it difficult to transport and prepare RM for further processing [1]. Numerous studies have found that RM contains increased amounts of iron, aluminum, gallium, vanadium, scandium and rare earth metals. In addition, the composition of the present RM carbonate and sodium hydroxide [2].

Given the importance of the problem of waste disposal, many ways of their disposal are proposed. Known technical solutions can be divided into three groups: hydrometallurgical, pyrometallurgical and combined. In the monograph [2] most promising specified block technology, including a preliminary separation of the components of the slurry by application of beneficiation techniques. In other works, for example [3–5], pyrometallurgical methods associated with obtaining cast iron (ferrosilicon) and calcium aluminate slag can be recognized as the most effective. The distinctive features of the developed methods are their multi-stage nature, which requires significant investment, as well as low quality of raw materials and products. In particular, during the pyrometallurgical processing of RM, the content of iron in the RM is not sufficient for its effective extraction, and in hydrometallurgical – iron is either not released at all or converted into a product of insufficient quality.

No less difficult task of waste disposal of ferrous metallurgy is oily rolling scale (OMS). In terms of iron content (65–75 %), it is a good raw material for the production of cast iron, steel and iron powders. The difficulty of its processing lies in the presence of residues of rolling grease. Part of the oil is in a free state and can be removed by known methods. The other part (3–5 % of the scale mass) is chemically bound to the surface of the material due to oxidation of the limiting hydrocarbons (the lubricant base). In the known methods of utilization of scale the organic compounds located on its surface are removed only by heat treatment. In this case, the organic component is either burned to form gases and carbon black or converted into condensate consisting of a wide range of organic compounds. In both cases, the disposal of OMS is significantly complicated [6].

Thus, despite numerous studies and tests of leading organizations, the problems of processing of RM and OMS still remain one of the most urgent in the field of processing of man-made waste. The authors search for technical solutions for the analysis of literary sources and patents in the field of processing of RM and OMS. A new approach to the disposal of the above-mentioned waste has been developed [7]. Its essence lies in the joint processing of these man-made waste to obtain a product suitable for extracting the main components by melting iron and alumina slag. The following can be considered prerequisites for a new approach to the disposal of RM and OMS:

- Oxidized organic compounds (e.g., fatty acids and their salts) to the water-soluble compounds in the presence of alkali [6]. Since the composition of the RM includes sodium oxide in the form of sodium carbonate and hydroxide, it is advisable to use to remove oxidized iron-containing salts of fatty acids from the scale. The mass ratio of scale and red mud in the mixture should be such that the iron content in the final product is in the range of 50–55 %, i.e. meets the requirements for raw materials smelting iron.
- Red mud possesses good binding properties for agglomerating particulate iron-containing raw materials [7].
- In the Ural region focused business, with heaps of oily scale and red mud, as well as companies processing iron ore and bauxite with additions of blast process of obtaining two marketable products – cast iron and calcium aluminate slag, and then processed on high-alumina cement.

The greatest interest as a promising object is the Kamensk-Ural industrial hub, where the Ural aluminum and Sinar pipe plants are located. The first of them has several slime silos, and the second one has a dump of a fine fraction of oiled rolling scale, which is not suitable for returning to the iron production cycle through agglomeration due to the high content of organic matter.

## 2. Experimental Part and Discussion of Results

Physical and chemical properties of technogenic wastes have been experimentally studied to assess the joint processing of RM and OMS with the help of modern techniques and equipment [8–12], including the use of equipment of the “Ural-M” Center for collective use. To determine the chemical composition of the used X-ray fluorescence spectrometer “S4 Explorer”, the phase composition X-ray diffractometer “XRD 7000C”, granulometric composition of the laser device “ANALYSETTE 22 NanoTec”, specific surface area – gas adsorptive analyzer “TriStar 3020”, scanning electron microscope “Carl Zeiss EVO 40”.

It is established that the main components of RM (table 1, sample 1) are: iron (35.7 %) in the form of hematite and complex hydroaluminate (Figure 1), calcium (11.0 %) in the form of calcite and hydroaluminate, aluminum (6.8 %), silicon (4.7 %) in the composition of hydroaluminate, sodium (2.8 %) in the composition of hydroaluminate, carbonate and hydroxide, and finally, titan (2.5 %) in the form of rutile. It is confirmed that, in addition to the listed components, there are a number of other elements in quantities not exceeding

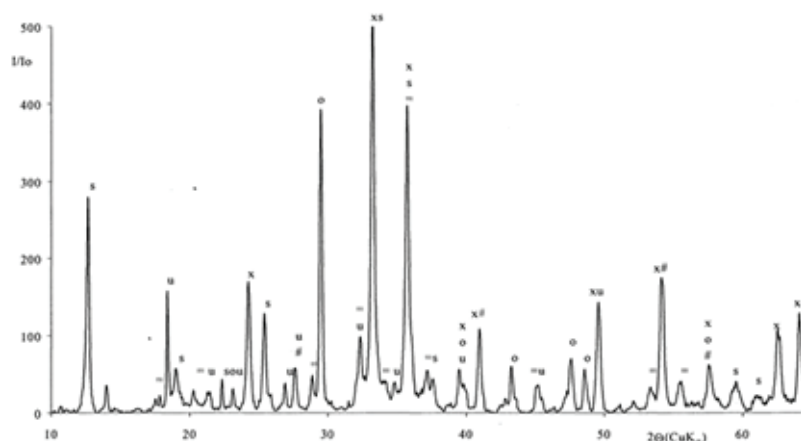
TABLE 1: The compositions of red mud and oily rolling scale.

Red mud 1		Red mud 2		Oily rolling scale 3		Oily rolling scale 4	
Element	Content, %	Element	Content, %	Element	Content, %	Element	Content, %
Al	6.80	Al	7.03	Al	1.27	Al	1.12
		As	0.029				
Ca	11.04	Ca	10.95	Ca	0.537	Ca	0.504
Ce	0.079	Ce	0.076				
Cl	0.037	Cl	0.038				
Co	0.075	Co	0.082	Co	0.163	Co	0.15
Cr	0.0363	Cr	0.0362	Cr	0.234	Cr	0.251
Cu	0.0679	Cu	0.0735	Cu	0.186	Cu	0.18
Fe	35.72	Fe	36.31	Fe	71.01	Fe	70.83
		Ga	0.0046				
K	0.166	K	0.147	K	0.0772	K	0.0738
Mg	0.55	Mg	0.547	Mg	0.749	Mg	0.683
Mn	0.469	Mn	0.478	Mn	0.636	Mn	0.609
				Mo	0.0251	Mo	0.0228
Na	2.76	Na	2.31	Na	0.21	Na	0.881
Nb	0.0071	Nb	0.0072				
O	33.30	O	33.20	O	19.40	O	20.30
P	0.338	P	0.36	P	0.48	P	0.49
Pb	0.021	Pb	0.021				
S	0.966	S	0.582	S	0.244	S	0.049
Si	4.65	Si	4.71	Si	2.87	Si	2.80
Sr	0.181	Sr	0.188				
Ti	2.516	Ti	2.563	Ti	0.0255	Ti	0.0244
V	0.047	V	0.049	V	0.014	V	0.014
Y	0.0285	Y	0.0305				
Zn	0.046	Zn	0.045	Zn	0.0328	Zn	0.0285
Zr	0.115	Zr	0.124				

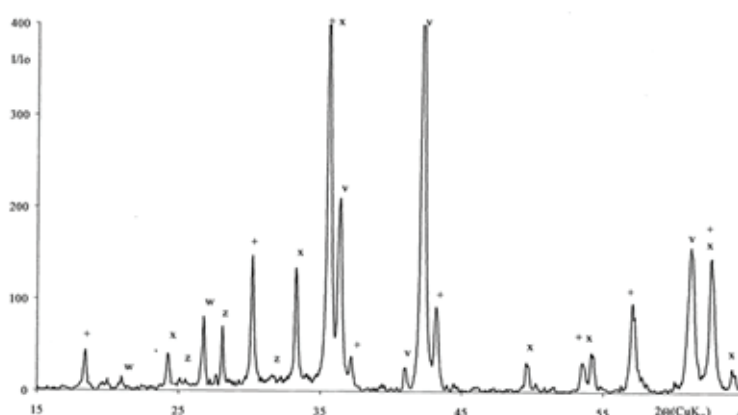
tenths of a per cent. The humidity of the red mud sample taken from the slope of the red mud storage of the Urals aluminum plant was 11.9 %.

The main components of OMS (table 1, sample 3) are: iron (71 %) in the form of (Figure 2) magnetite, vustite and hematite with a very small amount of fayalite. The content of silicon (in the form of quartz), aluminum and phosphorus (not forming separate phases) are in the range of 1–3 %. Within the same limits is the sum of other impurities (chromium, manganese, cobalt, copper). Humidity OMS, taken from the dump of the Sinarsky pipe plant amounted to 16.3 %, the content insoluble in water of organic matter – 4.0 %.

Granulometric composition of RM (Figure 3, table 2) characterized by high dispersion. With an average diameter of 1.6  $\mu\text{m}$ , all particle sizes are in the region of 0.5–12  $\mu\text{m}$



**Figure 1:** Diffraction pattern of red mud 1 (before treatment): x –  $\text{Fe}_2\text{O}_3$ ; o –  $\text{CaCO}_3$  (calcite); s –  $(\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al})_3(\text{Si}, \text{Al})_2\text{O}_5(\text{OH})_4$ ; –  $\text{Ca}_3(\text{Fe}_{0.87}\text{Al}_{0.13})_2(\text{SiO}_4)_{1.65}(\text{OH})_{5.4}$ ; u –  $\text{Ca}_3\text{Na}_2\text{Si}_6\text{O}_{16}$ ; # –  $\text{TiO}_2$  (rutile).

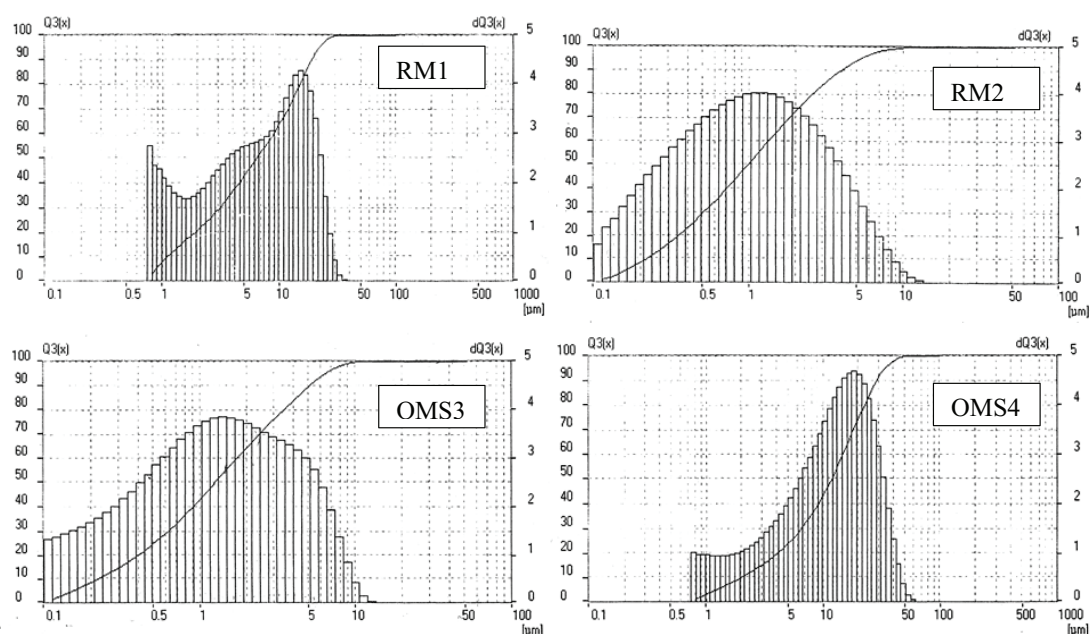


**Figure 2:** Diffractogram of scale 3 (before treatment): m –  $\text{FeO}$ ; + –  $\text{Fe}_3\text{O}_4$ ; x –  $\text{Fe}_2\text{O}_3$ ; w –  $\text{SiO}_2$  (quartz); l –  $(\text{Fe}, \text{Mg})_2\text{SiO}_4$ .

The particle size distribution is close to normal, except for the particle area less than  $1.2 \mu\text{m}$ . Granulometric composition of OMS (Figure 3, table 2) different complexity. With an average diameter of  $8.6 \mu\text{m}$ , the particle size distribution has maxima of  $0.9 \mu\text{m}$  and  $15 \mu\text{m}$  and a minimum of about  $1.2 \mu\text{m}$ . The difference in dispersion is reflected in the specific surface of both materials. She is from  $\text{RM } 23.7 \text{ m}^2/\text{g}$ , and OMS–  $1.9 \text{ m}^2/\text{g}$ .

The change in the properties of waste after exposure to aqueous solutions of alkalis and acids, neutralizing the influence of organic (OMS) and alkaline (RM) surface compounds that prevent separate disposal. It is shown that the neutralization of aqueous suspension with HCL solution leads to the removal of the alkaline film from the surface. Treatment of OMS with an aqueous solution of sodium hydroxide provides (Figure 3, table 2, sample 4) destruction of aggregates of particles bonded by water insoluble oxidation product of industrial oil. As a result of exposure to reagents, there is a decrease in the content of water-soluble components in the processing products. Changes in the

composition of the latter are reflected in the granulometric compositions. In this case, the average particle size of RM and OMS (table 2) increase to 2 and 14  $\mu\text{m}$  respectively, the specific surface area to 25.7 and 2.3  $\text{m}^2/\text{g}$ . particle size Distribution in RM (Figure 3, sample 2) practically does not change, and at OMS (Figure 1, sample 4) – approximately 5 and 10 % smoothed maximum and minimum in areas less than 0.5 and 15  $\mu\text{m}$ . Similar effects are observed in the joint aqueous leaching of oily scale and red mud, which has sodium hydroxide in its composition. The study can serve as a basis for further development of promising technology for the joint processing of red mud and oiled rolling scale.

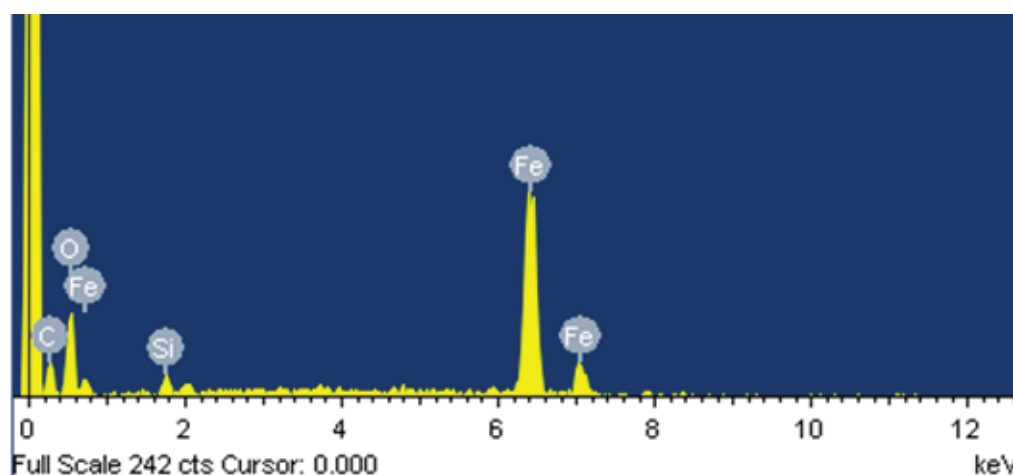


**Figure 3:** The distribution of particle size in samples RM 1 and OMS 3 – before treatment, RM 2 and OMS 4 – after treatment.

TABLE 2: Statistical values of particles in Figure 3.

Parameter	particle Diamete, $\mu\text{m}$			
	RM 1	RM 2	OMS 3	OMS 4
arithmetic mean	1.629	2.037	8.585	14.022
geometric mean	0.969	1.173	5.526	9.580
average harmonic	2.386	2.905	11.125	17.543
average quadratic	0.570	0.622	3.164	5.286

Electron microscopy of the surface layer of ZPO (Figure 4) showed (table 3) that its components are mainly iron, oxygen and carbon. These elements appear to form iron stearate.



**Figure 4:** Electronic spectrum of the surface layer of the OMS.

TABLE 3: Elemental composition of the surface layer of OMS.

Element	% (mass)	% (atom)
C	27.26	51.72
O	17.80	25.34
Si	1.32	1.07
Fe	53.62	21.87
Total	100.00	100.00

### 3. Summary

1. Based on the analysis of the literature data in the field of useful use of red mud and oily mill scale, a new direction of utilization is formulated: the joint processing of these wastes with the task of obtaining liquid products.

2. With the help of modern methods and equipment, a study of the physical and chemical properties of red mud and oily mill scale was carried out. In particular, information about the elemental, phase and granulometric composition of both types of waste, as well as their specific surface area.

3. It is confirmed that the main components of red mud are difficult hydroaluminates, calcite, and hematite, oily mill scale – magnetite. The peculiarity of red mud is excessive alkalinity, and oily scale-the presence of insoluble organic matter.

4. Both types of waste are highly dispersed. Red mud has an average particle size of 1.6  $\mu\text{m}$  in the range of 0.5–12  $\mu\text{m}$ , and scale – 1.2  $\mu\text{m}$  in the range of 0.9 to 15  $\mu\text{m}$ . It was found that the neutralization of alkali red mud with hydrochloric acid, and scale-when treated with an alkaline solution, the average particle size increases, respectively, to 2 and 14  $\mu\text{m}$ . At the same time the specific surface increases: red mud from 23.7 to 25.7, and scale 1.9 to 2.3  $\text{m}^2/\text{g}$ .



## Gratitudes

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